

THEORY OF INORGANIC NANOPARTICLE DELIQUESCENT EFFLORESCENCE



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1. Introduction

Following the deliquescent* uptake of water by inorganic aerosols, particles can easily grow to several times their original size. This growth has important consequences for the representation of aerosols in models, including the increased light scattering and cloud activation efficiencies that affect aerosol direct and indirect forcing.

Laboratory measurements have advanced to the point that measurements of the deliquescence transition have been made on particles ranging from bulk size down to a few nanometers in diameter. These measurements can lead to better predictions of how particles grow from the nanometer scale to the climate-impacting size regime. The theory of deliquescence, for example understanding how dry particle size and composition determine deliquescence relative humidity, DRH, is not nearly as well developed - there are even different conditions used in the literature to predict when deliquescence occurs!

This poster outlines a new, unified theory of deliquescence and efflorescence** processes and makes connections to Kohler theory and the theory of nucleation.

* deliquescence: to dissolve and become liquid by absorbing moisture from air

** efflorescence: formation of solids by evaporation of water

2. Under What Conditions Does Deliquescence Occur?

In bulk systems the deliquescence from salt particle to solution drop occurs at DRH equal to the RH over a saturated salt solution, and the drop concentration equals that of the saturated solution. In this case the free energy of the initial state A (dry or thinly coated salt particle plus vapor) equals that of the final state B (the saturated solution drop plus vapor). Thus at deliquescence:

$$G_A(DRH) = G_B(DRH) \quad (1)$$

Eq. 1 has been used in several papers to predict DRH even for salt particles of several nanometers size [1,2]. However there is no a priori reason why Eq. 1 should apply outside of the bulk regime. Another paper [3] presents a different criterion, which is much closer to the thin layer criterion (TLC) presented here. Our criterion is that at the DRH: (1) the chemical potential of water in the adsorbed solution layer equals the chemical potential of vapor and (2) the chemical potential of salt in the un-dissolved core equals the chemical potential of salt in the adsorbed layer. Thus the two conditions:

$$\begin{aligned} \mu_w(soln) &= \mu_w(vapor) \\ \mu_{salt}(soln) &= \mu_{salt}(core) \end{aligned} \quad (2)$$

Conditions 1 and 2 are equivalent in the bulk limit of large dry particle size.

3. Thin-Layer Criterion (TLC)

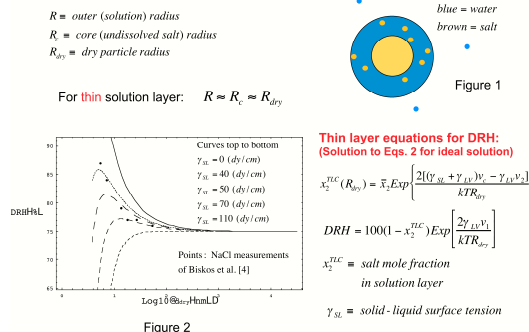
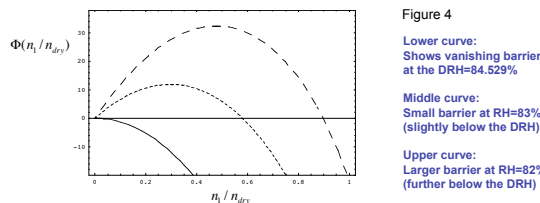


Fig. 2 shows that the DRH can either increase or decrease with decreasing dry particle size. Factors that favor a decrease in DRH are high salt-solution interfacial tension, high molecular volume in the crystalline phase, and small dry particle size.

Model parameters:

Thermodynamic properties, with the exception of \bar{x}_2 , are taken from Mirabel et al. [1] for deliquescence of a generic sodium chloride crystal: $v_1 = v_2 = 3.03 \times 10^{-23} \text{ cm}^3$, $v_c = 4.48 \times 10^{-23} \text{ cm}^3$, $\gamma_{lv} = 70 \text{ dy/cm}$, $T = 300 \text{ K}$. We set $\bar{x}_2 = 0.25$ to match the bulk DRH of 75% measured by Biskos et al. [4].

5. Nucleation Barrier to Deliquescence



The work of particle formation, $W(n_i/n_d)$ at any specified RH has a simple expression in terms of the equilibrium relative humidity RH_{eq} plotted in Fig. 2. For $\Phi(n_i/n_d) = W(n_i/n_d)/kT$:

$$\Phi(n_i/n_d) - \Phi(0) = -n_d \int_0^{n_i/n_d} \ln[RH/RH_{eq}(z)] dz.$$

Theory predicts that only for particles approaching 1nm diameter will it be possible to see deliquescence significantly below the DRH.

4. Thermodynamics of Particle-Droplet Transformation

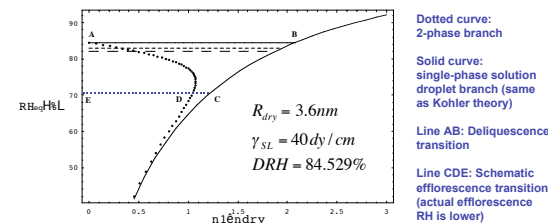


Figure 3. Equilibrium RH from solving Eqs. 2 where n_i is the number of water molecules and n_{dry} is the fixed number of salt molecules in the particle/droplet. Dotted curve shows the 2-phase core-solution layer particle (Fig. 1) for undissolved core radius ranging from the dry particle radius (3.6nm) down to 1nm where most of the salt has been dissolved. Condition D describes the critical salt nucleus in unstable equilibrium with supersaturated solution. Line CD is the homogeneous nucleation transition responsible for efflorescence to dry salt, E, depicted here at elevated RH for clarity. The actual transition occurs when the two branches are much closer together (below about 50% RH).

The solid horizontal line shows the deliquescence transition at 84.529% RH. Note that this condition lies along the second from top DRH curve in Fig. 2 at dry particle diameter equal to 7.2nm. The horizontal dashed lines at RH values of 83 and 82% show deliquescence slightly below the DRH. Under these conditions deliquescence becomes a nucleation process requiring transition over corresponding higher free-energy barriers (Fig. 4).

6. Summary

A new theory for the deliquescence of nano-sized particles is described based on local equality of chemical potentials (Eqs. 2) rather than on equality of initial and final state free energies (Eq. 1). These are equivalent only in the bulk limit. The more general criterion based on Eq. 2 is recommended. Calculations have been carried out using measured salt activities (non-ideal solution thermodynamics). These show qualitatively similar results and will soon be reported.

Acknowledgements

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References

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